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Copper(II)-Catalyzed Oxidative Coupling of 2,6-Dimethylphenol

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The oxidative coupling reaction of 2,6-dimethylphenol catalyzed by the copper(II) nitrate–acetonitrile complex has been studied. C–C coupling product, 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone, was selectively yielded with the present catalytic system. The influence of certain reaction variables, copper(II) nitrate concentration, solvent composition, and H_2O addition, on the C–C coupling yield was investigated. The kinetics of the oxidative coupling reaction were first order in copper(II) catalyst concentration and in 2,6-dimethylphenol concentration, respectively. These observations were in accord with the hypothesis that the rate-determining step was between active copper(II) catalyst and 2,6-dimethylphenol. The intermediate copper(II)–phenoxo complex formed must then proceed to yield the C–C coupling product and Cu(I) complex which would be reoxidized rapidly with oxygen. The C–C coupling activity of the copper(II) catalyst was specific in the case of pyridine addition. The variation of C–C coupling product yield with piperidine or diethylamine addition was found to show the similar variation as pyridine was added to the copper(II) complex. On the addition of increasing amounts of piperidine or diethylamine to the catalytic system C–O coupling product, poly(2,6-dimethylphenylene oxide), was obtained, in contrast to pyridine addition by which showed no C–O coupling formation. Thus it was indicated that some amine addition in the copper(II)–acetonitrile system affected the coupling mode of 2,6-dimethylphenol. Mechanistic aspects are proposed to explain the course of C–C coupling of 2,6-dimethylphenol with copper(II) nitrate–acetonitrile catalytic system.

INTRODUCTION

Phenol coupling is an important synthetic tool and an essential step in the biosynthesis of many alkaloids and other natural products (*1*). The reagents most extensively employed to effect this coupling (ferricyanide, ferric chloride, MnO_2, PbO_2, Ag_2O) often suffer from poor selectivity and usually give a mixture of quinones, dimers and polymers, the product distribution varying widely with the nature of the reagent.

Oxidative coupling of sterically hindered 2,6-dialkylphenols have been performed with various series of reagents, e.g., vanadium tetrachloride (*2*), isoamyl nitrate (*3*), silver carbonate/cerite (*4*), periodic acid (*5*), and PbO_2 (*6*). In 1959 Hay *et al.* (*7*) reported that certain 2,6-disubstitute phenol reacted with oxygen in the presence of an amine complex of copper salt as catalyst to yield high molecular weight polyphenylene ethers. The corresponding diphenoquinones were by-products. The selectivity to a particular product depends upon the catalyst, solvent, and the phenolic compound used. It was reported in the previous papers (*8*) that the oxidative displacement polymerization of 2,4,6-tribromophenol was achieved by employing copper(II) nitrate–acetonitrile catalytic

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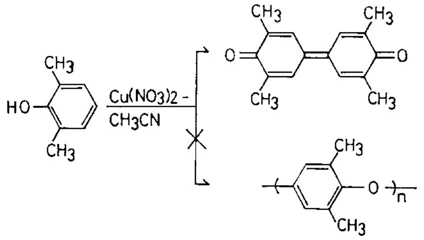
system. With this homogeneous copper complex, the poly(dibromophenylene oxide) has been obtained selectively. This copper(II)–acetonitrile complex has been found to act as an one-electron transfer reagent of phenol derivatives from the esr observation of sterically hindered phenol with copper(II) nitrate–acetonitrile system. In seeking to extend the application of copper(II)–acetonitrile complex as a catalyst for the oxidative coupling reaction, it is of interest to use 2,6-dimethylphenol and to investigate the activity and/or the coupling mode for this phenol. Although a number of catalytic oxidations for the oxidative coupling of phenol derivatives have been reported, there is little information on the kinetic treatment of the reaction system (*9*).

In this paper, we present the results of a study on the oxidative coupling reaction of 2,6-dimethylphenol with copper(II) nitrate in acetonitrile. C–C coupling product, the corresponding diphenoquinone, was obtained selectively with copper(II) nitrate–acetonitrile catalytic system.



SCHEME 1

The nature of the reaction was studied under a variety of reaction conditions, and the activity was sensitive to certain reaction conditions. From the kinetic treatment of the reaction with copper (II) nitrate–acetonitrile system, the dependences of 2,6-dimethylphenol and copper(II) nitrate on the rate were investigated. Furthermore, the effect of some amine addition on the activity and the coupling mode of the reaction was investigated. The coupling mode of 2,6-dimethylphenol was found to show a specific behavior by the addition of amines.

EXPERIMENTAL METHODS

Melting points were taken on a Mitamura Riken melting point apparatus and were uncorrected. Infrared spectra (ir) were obtained on Hitachi EPIG 2 and Hitachi 215 infrared spectrophotometers. Visible spectra were measured using Hitachi EPS-3 and Hitachi 139 spectrophotometers. Nuclear magnetic resonance (nmr) spectra were obtained on a JEOL PS-100 spectrometer using chloroform-*d* as a solvent and tetramethylsilane (TMS) as an internal reference. Elemental analyses were performed by the Microanalysis Center, Kyoto University.

Materials

2,6-Dimethylphenol was recrystallized from *n*-hexane. Reagent grade hydrated copper(II) nitrate was obtained commercially and used as received. Acetonitrile used was dried over BaO for 24 hr and then distilled. Pyridine, diethylamine, and piperidine were purchased in the guaranteed quality and checked for impurities by vapor phase chromatography. Methanol was refluxed over powdered Mg and then distilled. 3,3′,5,5′-Tetramethyl-4,4′-biphenol was synthesized by reduction of the corresponding diphenoquinone with zinc powder in acetic acid (*10*).

Oxidative Coupling of 2,6-Dimethylphenol with Copper(II) Nitrate–Acetonitrile Catalyst

The oxidations of 2,6-dimethylphenol were performed by vigorous agitation of the homogeneous copper(II) complex catalyst in an oxygen atmosphere at a controlled temperature. In a typical experiment, copper(II) nitrate (0.04 *M*) was dissolved in 50 ml of acetonitrile and 2,6-dimethylphenol (0.2 *M*) was added to the catalyst.

The oxidation was started at 30°C in an oxygen atmosphere with the reaction vessel equipped with a mechanical stirrer, a gas-inlet tube and a condenser. The reaction was terminated after 1 hr. The reaction mixture was cooled in an ice bath and the resulting red crystals were filtered off, washed several times with chilled methanol, dried over silica gel under reduced pressure and weighed (40% yield). The filtrate was concentrated on a rotary evaporator. The residue was then extracted with benzene. The benzene layer was filtered, and stripped on a rotary evaporator. The resulting crystals were identified as 2,6-dimethylphenol, starting phenol, from its infrared spectrum. The red crystalline product resulted was identified as 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone.

Anal. Calcd for $C_{16}H_{16}O$: C, 79.97; H, 6.71. Found: C, 79.85; H, 6.68.

The nmr spectrum consisted of a singlet at δ 7.70 (phenyl H), a singlet δ 2.16 (CH_3) in the approximate ratio 1:3. The ir spectrum (KBr tablet) was identical with the authentic diphenoquinone obtained with copper(I)–pyridine system.

Oxidative Coupling of 2,6-Dimethylphenol with Amine Added Copper(II) Nitrate–Acetonitrile Catalyst

Except amine addition, the oxidation reactions were performed in the same manner described above. In the case that the corresponding polyphenylene oxide was obtained as a product by the method of some amine addition to the catalyst, the reaction mixture was poured into methanol containing a small amount of conc. HCl. The polymer precipitate was filtered, washed with methanol and dried. The polymer was identified as poly(2,6-dimethylphenylene oxide) with the aids of its ir and nmr spectra.

Kinetic Treatments

Kinetic studies were carried out in a constant-pressure type gas absorption equipment consisting of a reaction vessel with a magnetic stirrer connected to a gas buret and a U-tube manometer. The oxygen pressure was maintained constant at atmospheric, regulated by a gas stocker from a gas which was evolved by electrolysis of water. The electrolysis was controlled by an electric relay. The reaction vessel was attached with a pressure-equalized dropping funnel, in which acetonitrile solution of copper(II) nitrate was added into reaction vessel. The whole reaction system, which was thermostated at 25°C was saturated with oxygen gas for 40–60 min under vigorous stirring, and then catalyst solution was added to the phenol solution in the vessel from the dropping funnel after equilibrium had been reached. The oxygen consumption at constant pressure (usually 1 atm) was measured for certain time interval.

RESULTS

Oxidative Coupling Reaction of 2,6-Dimethylphenol

The particular system chosen for study was the oxidation of 2,6-dimethylphenol in solution under oxygen gas at atmospheric pressure using a catalyst derived from copper(II) nitrate and acetonitrile. Results concerning the effect on product yield was obtained for the concentration of copper(II) nitrate as shown in Fig. 1. Copper(II) nitrate–acetonitrile catalytic system was found to act as a selective C–C coupling reagent for 2,6-dimethylphenol. The C–O coupling product, poly(2,6-dimethylphenylene oxide), was not yielded by the oxidation of 2,6-dimethylphenol with copper(II) nitrate–acetonitrile system. As shown in Fig. 1, the yield of 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone, C–C coupling product, increased with the concentration of copper(II) nitrate up to 6×10^{-2} M, and the yield decreased at more than 6×10^{-2} M of copper(II) nitrate concentration. To test the role of oxygen 2,6-dimethylphenol was oxidized under nitrogen. With 2×10^{-2} M copper(II) nitrate concentration, no diphenoquinone was obtained, and the yield of diphenoquinone with 6×10^{-2} M copper(II) nitrate under a nitrogen atmosphere was 24% in comparison with 48% under an oxygen atmosphere as can be seen from Fig. 1. Both C–C coupling product yields under O_2 and N_2 atmosphere were nearly equal when 1:1 molar of copper(II) nitrate (2×10^{-1} M) was treated with 2,6-dimethylphenol.

Endres and co-workers (*11*) have made a study on the influence of certain variables on the relative rates of C–O and C–C coupling in the oxidation of 2,6-dimethylphenol in the presence of homogeneous catalysts derived from copper(I) chloride and pyridine under oxygen. With all other conditions held constant, it was found that the coupling mode was markedly affected by variation of the ligand ratio (mole ratio of pyridine to copper(I) chloride). In order to investigate the possibility of coupling mode change of 2,6-dimethylphenol with the present catalytic system by variation of the ligand ratio, oxidations of 2,6-dimethylphenol were carried out with the mixed solvents of acetonitrile and *o*-dichlorobenzene [2,6-dimethylphenol, 0.2 M; copper(II) nitrate, 0.03 M; reaction time, 1 hr; reaction temperature, 30°C; O_2 atmosphere]. The ligand ratios [CH_3CN/copper(II) nitrate mole ratio] were varied from 320 to 639 (pure acetonitrile solvent). Because of the limit of solubility of copper(II) nitrate, it was impossible to approach smaller ligand ratio. Compared to the copper(I) chloride–pyridine system, 2,6-dimethylphenol was selectively oxidized to the corresponding diphenoquinone with the present catalyst, in spite of variation of the ligand ratio conducted at the present study. The yields of diphenoquinone obtained under these reaction conditions were held approximately constant at 31–37%.

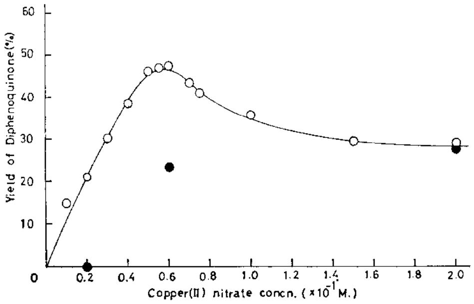


FIG. 1. Oxidation of 2,6-dimethylphenol with copper(II) nitrate–acetonitrile catalytic system. 2,6-Dimethylphenol, 0.2 M; solvent, 50 ml of acetonitrile; time, 1 hr; temp, 30°C; (○) O_2 atmosphere; (●) N_2 atmosphere.

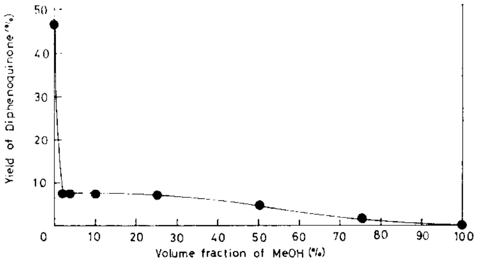


FIG. 2. Dependence of diphenoquinone yield on the volume fraction of methanol. 2,6-Dimethylphenol, 0.2 M; copper(II) nitrate, 0.6 M; solvent, 50 ml of (CH_3CN + MeOH); time, 1 hr; temp, 30°C; O_2 atmosphere.

The effect of methanol addition on the oxidation was studied. Figure 2 indicates the dependence of C–C coupling yield on the volume fraction of methanol. As indicated in Fig. 2, diphenoquinone yield was greatly diminished by the small amount of addition of methanol. Copper(II) nitrate in pure methanol solvent showed no activity for the present oxidation. Also in these mixed solvent systems, C–C coupling was favored and no C–O coupling product was yielded.

Table 1 demonstrates the effect of addition of H_2O on the yield of oxidation product. As is evident in Table 1, the yields of diphenoquinone were little affected by addition of small amount of H_2O.

It has been known that in the case of 2,6-disubstituted phenol, the correspond-

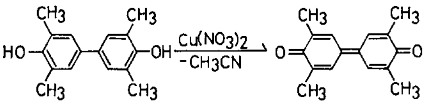
TABLE 1

Effects of H_2O Addition[a]

H_2O (mol)	Diphenoquinone yield (%)
None	48
0.017 (0.3 ml)	46
0.056 (1 ml)	50

[a] 2,6-Dimethylphenol, 0.2 *M*; copper(II) nitrate, 0.06 *M*; solvent, CH_3CN; time, 1 hr; temp, 30°C.

ing phenoxy radical generated with the catalytic oxidant would allow dimerization to the biphenol and subsequent oxidation of the biphenol would give the diphenoquinone. The oxidation of 3,3′,5,5′-tetramethyl-4,4′-biphenol with copper(II) nitrate in acetonitrile system was carried out.



A 4×10^{-2} *M* of diphenol was oxidized at 30°C with a 2×10^{-3} *M* of copper(II) nitrate in acetonitrile (25 ml) under oxygen for 1 hr. The corresponding diphenoquinone which was identified by its ir spectrum was obtained at 55% yield.

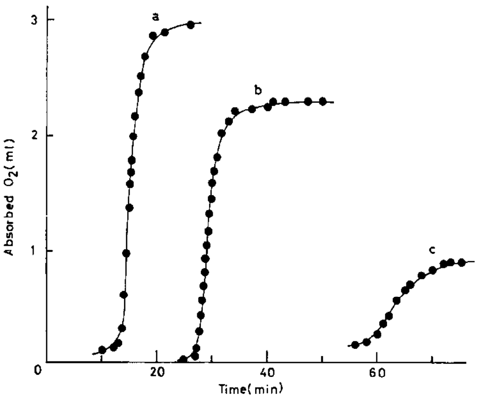


FIG. 3. Variation of amount of oxygen absorbed with reaction time. 2,6-Dimethylphenol, 7.5×10^{-2} *M*, solvent, acetonitrile; temp, 30°C; copper(II) nitrate: (a) 2.5×10^{-3} *M*, (b) 2.0×10^{-3} *M*, (c) 1.0×10^{-3} *M*.

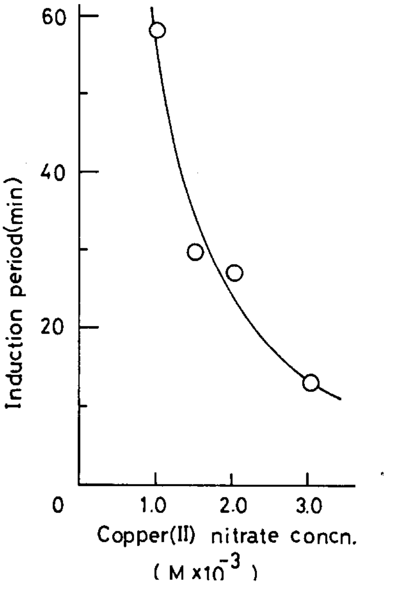


FIG. 4. Dependence of induction period on the concentration of copper(II) nitrate. 2,6-Dimethylphenol, 7.5×10^{-3} *M*.

Kinetics of Oxidation of 2,6-Dimethylphenol with Copper(II) Nitrate–Acetonitrile System

Some factors affecting the rate of oxidative coupling of 2,6-dimethylphenol with copper(II) nitrate–acetonitrile system were studied by measuring the amount of absorbed oxygen at constant pressure in a closed system at 25°C. It was first shown that the conditions could be established in which oxygen diffusion was not the rate-controlling process. Some oxygen absorption curves for oxidative coupling of 2,6-dimethylphenol with the present catalytic system are shown in Fig. 3. It is obvious from Fig. 3 that plots of oxygen consumed vs reaction time are typical S-shaped curves in the condition of catalyst concentration variation under constant phenol concentration. The relationship between the absorbed amount of oxygen and time under the variation of phenol concentration (catalyst concentration, constant) was also observed as similar S-type curve as Fig. 3. It may be worthwhile to note that the

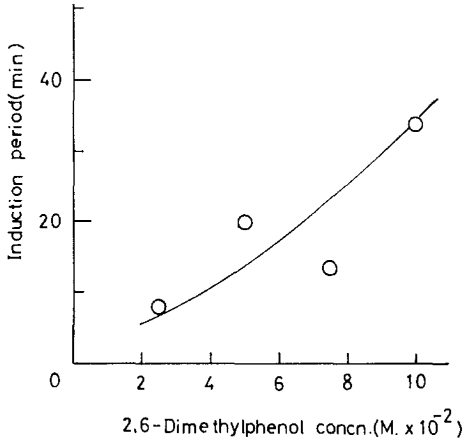


FIG. 5. Dependence of induction period on the concentration of 2,6-dimethylphenol. Copper(II) nitrate, 2.5 × 10^{-3} *M*.

induction period becomes longer with the decrease of copper(II) nitrate concentration as shown in Fig. 3. Figure 4 shows the dependence of induction period on the concentration of copper(II) nitrate. Although the clearcut dependence of induction period as shown in Fig. 4 was not observed for the variation of 2,6-dimethylphenol concentration, the increase of 2,6-dimethylphenol concentration had a tendency to make the induction period longer as shown in Fig. 5.

The rates of oxygen absorption were plotted for the concentrations of copper(II) nitrate and 2,6-dimethylphenol, respectively, as shown in Fig. 6a and b. As evidenced from Fig. 6, graphs of Fig. 6a and b are straight lines with slope equal to 1. This result indicates that the rate law is

$$r = k \cdot [\text{Cu(II) nitrate}]^1 \times [\text{2,6-dimethylphenol}]^1.$$

Where r and k are the formation rate of diphenoquinone and the apparent rate constant at 25°C, respectively. To obtain the value of k, the rate (r) was plotted against the product of the concentrations of copper(II) nitrate and 2,6-dimethylphenol. Value of the apparent rate constant (k) was found to be 7.69 liters/mol min from the slope of this linear rate plot.

Furthermore, the rate of diphenoquinone production was spectrometrically measured as a function of copper(II) nitrate concentration. The increase of $\lambda_{\max}$ of diphenoquinone, 412 nm, with reaction time was observed at 14°C in a 1-cm cell. The rate vs concentration of copper(II) nitrate relationship is shown in Fig. 7. The rate of diphenoquinone production was found to be dependent on the first order of the concentration of copper(II) nitrate, in accord with the case of the rate of oxygen absorption.

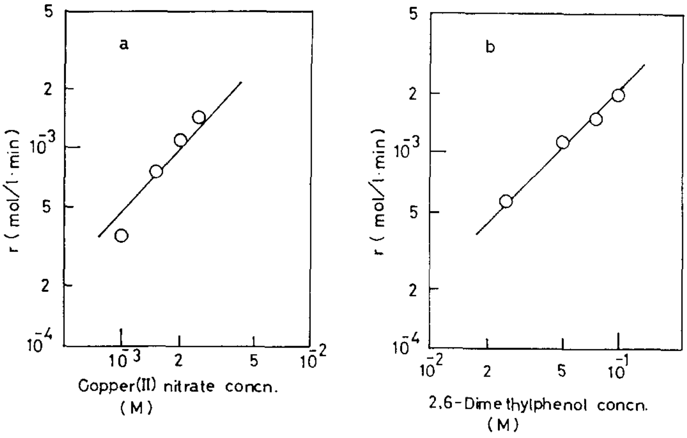


FIG. 6. Rate of oxygen absorption vs concentration of copper(II) nitrate and 2,6-dimethylphenol. Solvent, acetonitrile; temp, 30°C; (a) 2,6-dimethylphenol, 7.5 × 10^{-2} *M*; (b) copper(II) nitrate, 2.5 × 10^{-3} *M*.

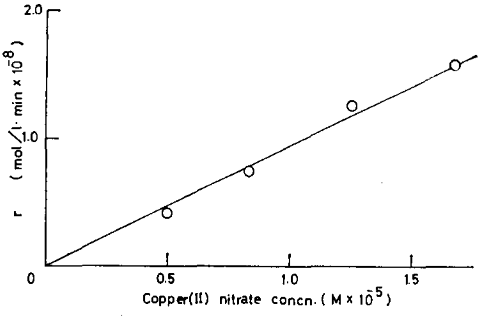


FIG. 7. Dependence of the rate of diphenoquinone production on the concentration of copper(II) nitrate. 2,6-Dimethylphenol, 6.67×10^{-5} *M*; temp, 14°C.

Effect of Amine Addition on the Oxidative Coupling of 2,6-Dimethylphenol

It is of interest to study the effect of some amine addition to copper(II) nitrate–acetonitrile catalyst system on the activity and/or coupling selectivity of oxidation of 2,6-dimethylphenol. As amine derivatives, pyridine, piperidine and diethylamine were used. Figure 8 indicates the effect of pyridine addition on the yield of coupling product. In the addition of pyridine to copper(II) nitrate–acetonitrile system, the whole catalytic system was held to homogeneous state. At first it is evident from Fig. 8 that only the corresponding diphenoquinone, C–C coupling product, was yielded as an oxidative coupling product in the case of pyridine addition. By contrast with the monotonous curve, the yield of diphenoquinone had the maximum value at the pyridine/copper(II) nitrate mole ratio of about 0.4. Further increase of pyridine to the catalytic system caused the remarkable decrease of the yield and no diphenoquinone was obtained at the pyridine/copper(II) nitrate ratio of more than 20. Thus by addition of a large excess of pyridine, the catalytic system was found to become inactive for the oxidative coupling reaction of 2,6-dimethylphenol.

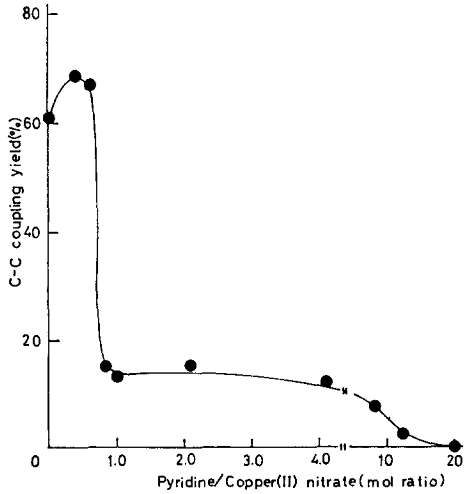


FIG. 8. Effect of pyridine addition on the oxidative coupling of 2,6-dimethylphenol. 2,6-Dimethylphenol, 0.2 *M*; copper(II) nitrate, 0.06 *M*.

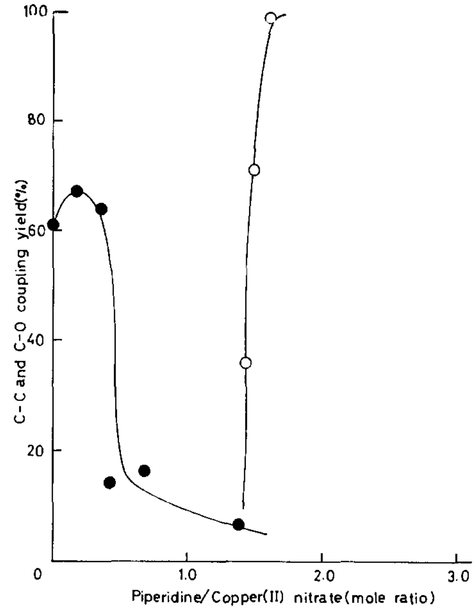


FIG. 9. Effect of piperidine addition on the oxidative coupling of 2,6-dimethylphenol. 2,6-Dimethylphenol, 0.2 *M*; copper(II) nitrate, 0.06 *M*; (●) C–C coupling; (○) C–O coupling.

Figures 9 and 10 show the effects of additions of piperidine and diethylamine, respectively, on the yield and/or coupling mode for the oxidative coupling of 2,6-dimethylphenol. By contrast with the case in pyridine addition, the addition of piperidine or diethylamine to the homogeneous catalytic system resulted in the heterogeneous state of the whole catalytic system. In the first place, it should be noted that by addition of piperidine or diethylamine the coupling manner, C–C and/or C–O coupling, changes clearly at the stage of certain ratio of amine added/copper(II) nitrate. The yield of diphenoquinone had the maximum value by addition of a small amount of piperidine but the further addition resulted in the conspicuous decrease of the yield and the activity for C–C coupling has been completely lost at more than about 1.5 of the piperidine/copper(II) nitrate mole ratio as shown in Fig. 9. This variation of the yield of C–C coupling product showed similar behavior as evidenced by the comparison with Fig. 9 and 10. But in the case of piperidine addition, C–O coupling product, poly(2,6-dimethylphenylene oxide), commenced to yield at the condition that C–C coupling activity was virtually lost. At the range of the piperidine/copper(II) nitrate mole ratio 1.4–1.5, the slight addition of piperidine caused the steep increase of C–O coupling product, polymer. The C–O coupling product was obtained in nearly quantitative yield at the ratio of about 1.6. The similar behavior of the coupling mode as Fig. 9 was observed by addition of diethylamine as shown in Fig. 10. Thus it was found that the addition of amine to the copper(II) nitrate–acetonitrile caused the variation of oxidation product yield and the change of coupling mode.

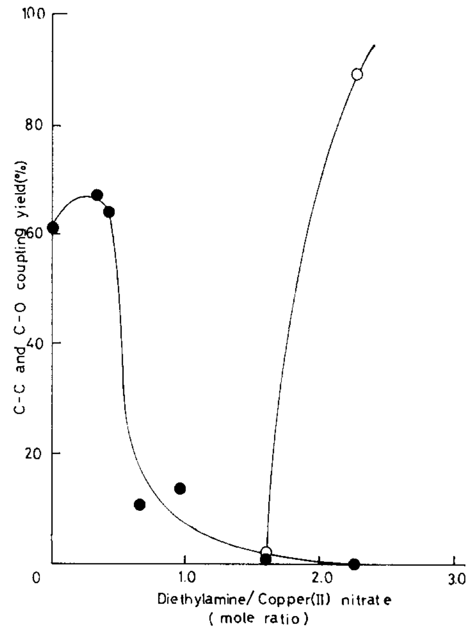


FIG. 10. Effect of diethylamine addition on the oxidative coupling of 2,6-dimethylphenol. 2,6-Dimethylphenol, 0.2 M; copper(II) nitrate, 0.06 M; (●) C–C coupling, (○) C–O coupling.

DISCUSSION

It has become apparent that copper(II) nitrate–acetonitrile catalyst was one of the effective catalysts for the selective oxidative C–C coupling of 2,6-dimethylphenol though the optimum condition was not sought at the present stage. In the place of copper(II) nitrate, the other copper(II) salts and some cobalt(II) salts were used as catalysts for the oxidative coupling of 2,6-dimethylphenol. The copper(II) salts [copper(II) chloride, copper(II) bromide, copper(II) perchlorate, and copper(II) acetylacetonato] and the cobalt(II) salts [cobalt(II) nitrate, and cobalt(II) acetylacetonato] used in acetonitrile at the present study were inactive for the oxidation of 2,6-dimethylphenol under the same reaction condition as using copper(II) nitrate as a catalyst. Thus only the copper(II) nitrate was found to be effective for the selective C–C coupling though at the present stage no definite reasons were evident.

Endres and his co-workers (*11*) have reported the dependence of the maximum rate of oxygen absorption on the ligand ratio (pyridine/CuCl mole ratio) in the copper(I) chloride–pyridine-catalyzed oxidation of 2,6-dimethylphenol. The rate was found to have one maximum value with the variation of the ligand ratio though little information on the reason was obtained. The dependence of copper(II) nitrate concentration on the diphenoquinone yield, with further high concentration of

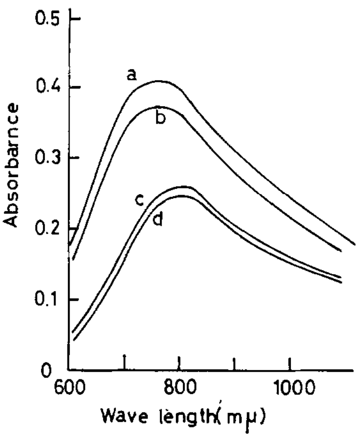
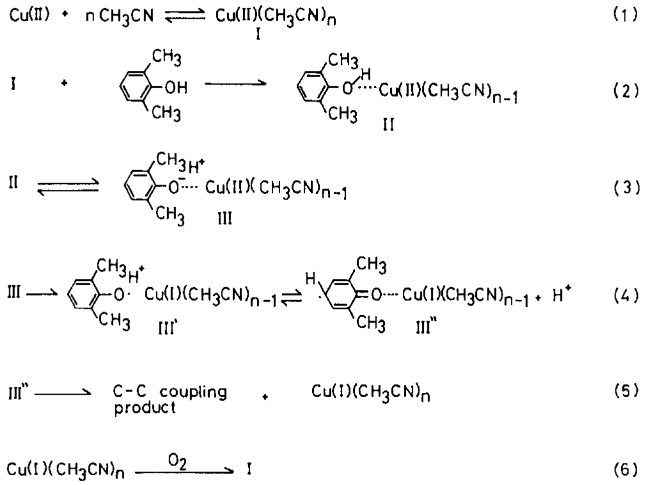


FIG. 11. Electronic absorption spectra of copper(II) complexes. Copper(II) nitrate, 0.01 *M*; solvent: (a) CH_3CN only, (b) $CH_3CN:CH_3OH = 49:1$ (vol%), (c) $CH_3CN:CH_3OH = 1:1$, (d) CH_3OH only.

copper(II) nitrate, the product yield was found to decrease inversely. This behavior may be interpreted in terms of the change of the catalyst composition. Initial increase of the copper(II) nitrate may cause the increase of active copper(II) species. Therefore an increase in the C–C coupling yield is observed. As enough copper(II) nitrate is added, the formation of inactive copper(II) complex such as binuclear or polynuclear species may become favorable and the yield of oxidation product may decrease. In order to investigate the effect of ligand ratio on the coupling mode, the reaction with constant copper(II) nitrate concentration in acetonitrile–*o*-dichlorobenzene mixed solvent was studied. The yields of C–C coupling product were nearly equal and no C–O coupling product was yielded in spite of the variation of acetonitrile/copper(II) nitrate mole ratio, in contrast to the copper(I) chloride–pyridine catalyst.

It was reported (*8*) that the yield of poly(dibromophenylene oxide) obtained by the oxidative displacement reaction of 2,4,6-tribromophenol with copper(II) nitrate in acetonitrile–methanol mixed solvent was remarkably diminished in comparison with pure acetonitrile solvent. It is evident from Fig. 2 that the presence of methanol in the catalytic system acts as an important inhibitor for the present oxidation. In order to gain a better understanding of the effect of methanol, the electronic absorption spectra of the catalyst system were observed at room temperature. Figure 11 shows the variation of near-infrared spectra of copper(II) complex with the composition of solvent. With the increase of methanol fraction, λ_{max} of the spectrum shifts to longer wavelength and ϵ_{max} decreases. In the previous paper (*8*), it was found that the greater the catalytic activities of copper(II) complexes in the oxidative displacement reaction of 2,4,6-tribromophenol, the lower λ_{max} of the copper(II) complexes. It is interesting to note that the similar correlation between λ_{max} of copper(II) complex and reactivity is obtained for the present oxidative coupling reaction of 2,6-dimethylphenol. Thus the increase of ligand field of the copper(II) complex may cause the increase of its oxidizing power for phenol derivatives.

The kinetic data indicates that the rate-determining step in oxidative coupling reaction involves a reaction of copper(II) species with 2,6-dimethylphenol. As described above, since some copper(II) salts, other than copper(II) nitrate have no catalytic activity, we assume that nitrate groups play a unique role. It is well known that in copper(II) nitrate the bonds between copper(II) ion and anion part (nitrate ion), have stronger ionic character than the other copper(II) salts. Because of the ionic character in the bond between copper(II) ion and nitrate ion, active copper(II)–acetonitrile complexes may be more easily formed in the case of using copper(II) nitrate as a catalyst. Also, the dependence of induction period on the copper(II) nitrate concentration as shown in Fig. 4 seems to indicate that active catalytic species are formed by the interaction of copper(II) nitrate with acetonitrile. Also this nonlinear plot of induction period versus copper(II) nitrate concentration may suggest the formation of dimeric, or higher oligomeric copper(II) species which seem to be inactive for the present oxidation, in addition to monomeric copper(II) ones.



A reasonable mechanistic model for reaction with 2,6-dimethylphenol is given in Scheme 1, where **I** represents active catalytic species. The dependences of induction period on the concentrations of copper(II) nitrate and 2,6-dimethylphenol seem to affirm step (1) as the first step. Equation (6) is a reoxidation step of copper(I) complexes to active Cu(II) species with molecular oxygen that must occur after the rate-limiting step. Mechanistic details cannot be revealed by our kinetic evidence which only gives the composition of the intermediate phenoxo-copper(II)–acetonitrile complex for step (2). Phenol moiety of **II**, that was formed by the interaction of 2,6-dimethylphenol with active copper(II)–acetonitrile complex, **I**, may be ionized to phenolate anion and proton because of electron deficiency on oxygen atom of 2,6-dimethylphenol by the interaction with copper(II) ion as shown in **III**. The fact (*8*) that copper(II) nitrate–acetonitrile complex acts as a one-electron transfer oxidant for phenol derivatives as evidenced from the esr observation indicates that the corresponding phenoxy radical is generated by one-electron transfer process in **III**. The radical in **III″** is the resonance structure of phenoxy radical in **III′**. It is reasonable to consider that C–C coupling is markedly favored relative to C–O coupling by a preferential formation of **III″**.

It was found that the activity of the copper(II) catalyst is highly specific for the same amine addition. The effect of adding pyridine to the catalytic system is indicated in Fig. 7. It can be seen that the yield of C–C coupling product initially rises. The yield then decreases steeply with further pyridine addition. From the electronic absorption spectra of the copper(II) complex, it is evident that copper(II)–pyridine complexes which are considered to be inactive for the present coupling are formed by the pyridine addition into the acetonitrile solution of copper(II) nitrate. On the other hand free pyridine not coordinated with copper(II) ion is considered to act as a promoter of the phenoxide formation through hydrogen bonding between 2,6-dimethylphenol and pyridine. In fact, Fig. 12 shows that OH stretching absorption band of 2,6-dimethylphenol in pyridine

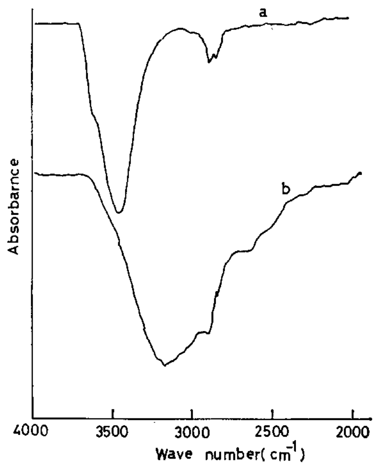


FIG. 12. Infrared spectra of OH absorption bands of 2,6-dimethylphenols in acetonitrile and pyridine solvents: (a) in acetonitrile, (b) in pyridine.

solvent has a lower wave number and a broader shape than that in acetonitrile solvent. The generation of phenoxide anions is considered to make the formation of the intermediate, copper(II)–phenoxide complex more easily. These competitive functions of pyridine may be responsible for the maximum yield of C–C coupling in the region of a slight pyridine addition. The cause of appearance of the maximum yield of C–C coupling in the case of the other amine addition may be also attributed to the reason described above. Though the oxidative coupling product was not yielded completely at the pyridine/copper(II) nitrate mole ratio of 20, in the case of piperidine or diethylamine, C–O coupling product, polyphenylene oxide, began to yield under the reaction condition that the activity for C–C coupling had not exhibited. It is particularly interesting to note that the active region for C–O coupling is clearly separated from that for C–C coupling reaction. Thus it is considered that the active copper(II) species for C–C coupling is converted to the active copper(II) species lead predominantly to C–O coupling with the addition of piperidine or diethylamine to copper(II)–acetonitrile system. In contrast to the case of pyridine, copper(II)–piperidine and copper(II)–diethylamine complexes that were formed at more than 1.5-2 of the amine/copper(II) mole ratio were indicated to function as a catalyst for C–O coupling reaction of 2,6-dimethylphenol. Although we have no definite experimental evidence at the present stage, it is believed reasonable to expect that the critical variables for coupling mode are those which would affect the structure of the catalytic copper(II) complex.

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